Propanol synthesis from CO_2, C_2H_4 and H_2 over Au-containing catalysts: Effect of support and K doping on activity and selectivity

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Introduction

Emissions of climate-relevant gases like CO_2 and the scarcity of natural resources are just two major problems modern chemistry is facing nowadays. Therefore, various approaches have been considered for CO_2 conversion to useful chemicals[1]. In the present contribution we introduce an alternative route for the synthesis of propanol from CO_2, C_2H_4, and H_2. Propanol can be easily further dehydrated to C_3H_6.

The idea behind our approach is the combination of heterogeneously catalyzed CO_2 conversion to CO through reverse water-gas shift (RWGS) reaction with the hydroformylation of the in situ produced CO with C_2H_4 to propanal on one catalyst. Supported Au nanoparticles (NP) are known to catalyze RWGS[2] and hydroformylation of olefins with CO[3]. This contribution demonstrates that Au-containing materials support both reactions simultaneously. In particular, we investigated the effect of support and K doping on oxo-selectivity (propanol and propanal), CO_2 conversion and non-desired C_2H_4 hydrogenation to C_2H_6.

Materials and Methods

All catalysts were prepared by deposition precipitation from $HAuCl_4$ with ammonia solution on different supports and incipient wetness impregnation of this precursor with a solution of KNO_3, followed by drying and calcination at 473 K. TiO_2_a (Anatase, BASF, 58 m^2/g), TiO_2_r (Rutile, Sachtleben, 93 m^2/g), and SiO_2 (Davisil, 232 m^2/g) were used as supports. The nominal Au loading is 2 wt.%.

Continuous flow experiments were carried out in a set-up equipped with an online gas chromatograph and 50 stainless-steel fix-bed reactors operating in parallel. The catalysts were characterized by XRD, TEM, ICP, BET, TAP (Temporal Analysis of Products), and in situ FTIR spectroscopy.

Results and Discussion

Table 1 shows $X(C_2H_4)$ and $X(CO_2)$ obtained over TiO_2_a- and SiO_2-based catalysts at 473 K and 2 MPa. The corresponding values for selectivity to CO and oxygenates (propanol plus propanal) are presented in **Figure 1**.

Table 1. Size of Au NP in supported Au-containing catalysts as well as conversion of C_2H_4 and CO_2. CO_2:H_2:C_2H_4:N_2 = 1:1:1:1, P = 2 MPa, τ = 45 g·min/L, T = 473 K.

	K-Au/TiO2_a				K-Au/SiO2				K-Au/TiO2_r	
K-loading /wt.%	0	1	2	3	1	2	3	4	0	1
$X(C_2H_4)$ / %	44.1	62.5	54.5	35.3	30.1	14.6	11.2	10.9	58.2	78.1
$X(CO_2)$ / %	3.6	3.3	1.2	0.8	0.7	0.8	0.8	1.0	4.9	4.8
$d_{Au\ NP}$ / nm	7.5*	4.5*	7*	10*	6.7#	17#	17#	20#	-	-

*determined by STEM (HAADF); #determined by XRD

For the K-Au/TiO2_a system, $X(C_2H_4)$ to C_2H_6 passes over a maximum of 62.5% at K loading of 1 wt.% and reaches 35% at the dopant concentration of 3 wt.%. The hydrogenation activity was found to be determined by the size of Au NP. In contrast to $X(C_2H_4)$, $X(CO_2)$ decreases continuously with an increase in K content due the formation of ionic carbonates upon CO_2 interaction with the catalysts. Such carbonates are too stable to quickly decompose to CO required for hydroformylation. In contrast to the conversion, the oxo-selectivity increases with K content and reaches 100% over K-Au/TiO2_a with K loading above 2 wt.% (**Figure 1**). When using TiO_2_r as support, $X(CO_2)$ is improved; Au/TiO2_r converted ca. 5% CO_2 compared to 3.6% over Au/TiO2_a with also slightly higher oxo-selectivity (21.3% vs. 18.1%). Promoting Au/TiO2_r with 1 wt.% K does not reduce $X(CO_2)$, but enhances the oxo-selectivity to 69.3%, thus resulting in the highest yield of oxygenates of 3.5% with respect to CO_2.
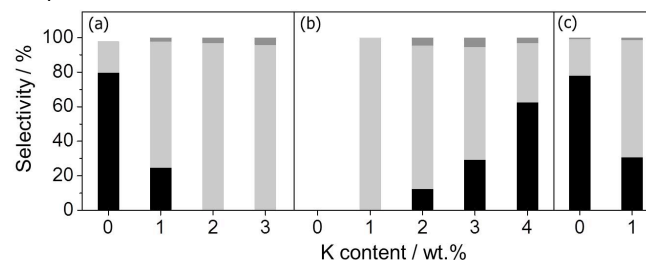

Figure 1. Selectivity to CO (black bar), propanal (dark grey), and propanol (light grey) on (a) K-Au/TiO2_a, (b) K-Au/SiO2, and (c) K-Au/TiO2_r. CO_2:H_2:C_2H_4:N_2 = 1:1:1:1, P = 2 MPa, τ = 45 g·min/L, T = 473 K.

It is worth mentioning that K-Au/SiO2 catalysts perform differently to K-Au/TiO2 counterparts. First of all, Au/SiO2 did not show any activity for the desired reaction, but hydrogenated C_2H_4 to C_2H_6 at about 51% conversion. Importantly, promoting with K significantly suppresses the hydrogenation activity down to 11% (**Table 1**). In addition, $X(CO_2)$ increases slightly but reaches only 1%. In terms of selectivity, 1K-Au/SiO2 showed a 100% propanol selectivity, which, however, decreases with a further increase in K loading (**Figure 1**). Based on the results obtained, we put forward that the activity and selectivity of supported Au-containing catalysts strongly depend on the kind of support, size of Au NP, and acidity which is tuned by promoting with K. This knowledge provides hints for design of novel catalysts with desired activity and most importantly selectivity.

Significance

This contribution shows for the first time the heterogeneous conversion of CO_2 with C_2H_4 and H_2 to C_3-oxygenates over Au-containing catalysts in one reactor. High propanol selectivity offers a facility for propene production through propanol dehydration.

References

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